CO_2 DIMER: FOUR INTERMOLECULAR MODES OBSERVED VIA INFRARED COMBINATION BANDS

JALAL NOROOZ OLIAEE, *Department of Physics and Astronomy, University of Calgary, Calgary, AB, Canada*; MEHDI DEHGHANY, *Department of Mathematics, Physics and Engineering, Mount Royal University, Calgary, Canada*; MOJTABA REZAEI, *Department of Physics and Astronomy, University of Calgary, Calgary, AB, Canada*; BOB McKELLAR, *Steacie Laboratory, National Research Council of Canada, Ottawa, ON, Canada*; NASSER MOAZZEN-AHMADI, *Physics and Astronomy/Institute for Quantum Science and Technology, University of Calgary, Calgary, AB, Canada*.

Study of the carbon dioxide dimer has a long history, but there is only one previous observation of an intermolecular vibration [1]. Here we analyze four new combination bands of $(CO_2)_2$ in the CO_2 ν_3 region ($\sim$2350 cm^{-1}), observed using tunable infrared lasers and a pulsed slit-jet supersonic expansion. The previous combination band at 2382.2 $\mathrm{cm}^{-1}$was simple to assign [1]. A much more complicated band ($\sim$2370 cm^{-1}) turns out to involve two upper states, one at 2369.0 cm^{-1}(B_u symmetry), and the other at 2370.0 cm^{-1}(A_u). The spectrum can be nicely fit by including the Coriolis interactions between these states. Another complicated band around 2443 cm^{-1}also involves two nearby upper states which are highly perturbed in so-far unexplained ways (possibly related to tunneling shifts).

With the help of new $ab\ initio$ calculations [2], we assign the results as follows. The 2369.0 cm^{-1}band is the combination of the forbidden A_g intramolecular fundamental (probably [1] at about 2346.76 cm^{-1}) and the intermolecular geared bend (B_u). The 2370.0 cm^{-1}band is the combination of the same A_g fundamental and the intermolecular torsion (A_u). This gives about 22.3 and 23.2 $\mathrm{cm}^{-1}$for the geared bend and torsion. The previous 2382.2 cm^{-1}band [1] is the allowed B_u fundamental (2350.771 cm^{-1}) plus two quanta of the geared bend (B_u), giving 31.509 $\mathrm{cm}^{-1}$for this overtone. The highly perturbed 2442.7 cm^{-1}band is the B_u fundamental plus the antigeared bend (A_g), giving about 91.9 $\mathrm{cm}^{-1}$for the antigeared bend. Finally, the perturbed 2442.1 cm^{-1}band is due to an unknown combination of modes which gains intensity from the antigeared bend by a Fermi-type interaction. Calculated values [2] are: 20.64 (geared bend), 24.44 (torsion), 32.34 (geared bend overtone), and 92.30 cm^{-1}(antigeared bend), in good agreement with experiment.

[1] M. Dehghany, A.R.W. McKellar, Mahin Afshari, and N. Moazzen-Ahmadi, *Mol. Phys.* **108**, 2195 (2010).
[2] X.-G. Wang, T. Carrington, Jr., and R. Dawes, private communication.